EXHIBIT D

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Catalysts' Role in Low-Gloss Hybrid Powder Coatings

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In this study, the crucial role played by catalysts in the preparation of low-gloss hybrid powder coatings using a reactive additive (styrene maleic anhydride copolymer) is described. First, the reactions that occur during the cure of epoxy/polyester hybrid thermoset powder coatings are reviewed. DSC measurements on model mixtures and fully formulated powder paints reveal relative reactivities and the role of catalysis on the various reaction steps. The gloss properties of the coatings are found to be closely tied to the presence of a catalyst. Several approaches to preparing powder coating formulations that exhibit fast cure kinetics, low-gloss appearance and excellent properties are described.

This paper is adapted from work originally presented at the 2001 International Waterborne, High-Solids, and Powder Coatings Symposium.

Table 1

Gloss Categories1	
Category Reading	**Gloss** (60-degree)
High	>85
Standard	70 to 85
Semi	40 to 70
Low	15 to 40
Matt	<15

Background

Gloss is a measure of the amount of light reflected from a surface at a given angle, and is expressed as a value between 0 and 100. Polished plate glass has a value of about 100, and a completely nonreflective surface has a value of 0. Low gloss coatings are typically measured as 60-degree gloss, although the 85-degree gloss is also sometimes used. The range of gloss readings are loosely divided into several categories, as shown in **Table 1.**

The chemical and physical properties of most major classes of powder coatings cure to give a level, glossy surface. However, for aesthetic and functional reasons, it is often desirable to have a powder coated surface with a low gloss, or matt finish. In such cases, gloss control may be achieved through many different

techniques, including the addition of inorganic fillers or organic waxes, the blending of powders of different reactivities or the use of certain reactive agents.

The choice of gloss control agent depends upon the level of gloss reduction desired and the chemistry of the powder coating. Fillers can give rough surfaces due to the protrusion of the fillers from the surface after baking, which disrupts reflected light. Waxes and other incompatible ingredients tend to segregate on the surface during baking, leaving circular voids or forming a film on the surface. The 60-degree gloss reduction of both fillers and waxes is limited to about 40. Blends of powders of differing chemistries/reactivities, as well as chemically reactive additives such as polycarboxylic acids or their acid salts are used to achieve low and matt finishes.

Low-molecular-weight styrene-maleic anhydride (SMA) resins are a family of anhydride and partial ester functionalized copolymers which have been widely used as gloss-reducing additives in thermoset epoxy powder coatings.2 Earlier studies suggest that a two-stage reaction process leads to the textures observed in low-gloss epoxy powder coatings containing SMA.1 In this mechanism, dicyandiamide (Dicy), another epoxy curative traditionally added to epoxy powder coatings, reacts at a different rate than the SMA curing agent, leading to two structural networks within the coating.1 In studies of a similarly reactive low-gloss additive, Lee et al3 observed low-gloss epoxy coatings during curing, and saw that the coarse surface morphology formed as the gel point of the coating was reached. After gelation, the surface roughness remained fairly constant even with further curing, although fine structure continued to develop past the gel point. This suggests that the low gloss texture is a consequence of morphology development during curing, and is not due to stress-induced texture development during the cooling of the powder coated surface.

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This study explores the use of SMA resins as gloss-reducing additives in the more complex epoxy/polyester hybrid powder coating system. In these formulations, the reactivities between three components—the epoxy resin, the polyester and the SMA anhydride and/or ester—must be balanced to give the different curing rates which create the low-gloss morphology. The curing kinetics of the three possible two-component combinations are explored first by DSC. Using these results, powder coating formulations are prepared and analyzed. These studies uncover the characteristics of the polyester resin and the SMA resins necessary to obtain low-gloss epoxy/polyester hybrid powder coatings.

The Experiment

Materials. Epon 2002 (Shell Chemical) is a standard "Type 3" Bisphenol A epoxy resin with EEW 675-760. Albester 2240 (McWhorter Technologies) is a high reactivity carboxyl-terminated 70/30 polyester resin with an acid number range of 35 to 45 mg KOH/g and a viscosity (at 200°C) of 6000 to 8000 mPa.s. Albester 2250 (McWhorter Technologies) is an uncatalyzed version of Albester 2240. Crylcoat 7401 (UCB Chemical) is a high reactivity carboxyl-functionalized 70/30 polyester resin with an acid number range of 32 to 40 mg KOH/g and a melt viscosity (at 160°C) of 25-42 Pa.s. Crylcoat 7402 (UCB Chemical) is the uncatalyzed version of Crylcoat 7401. Resiflow P-67 (Estron Chemical) is a flow-control agent. Huberbrite #1 (J. M. Huber) is a grade of powdered barium sulfate suitable for use in powder coatings.

SMA 3000 (Atofina Chemicals Inc.) is a low-molecular-weight copolymer of styrene and maleic anhydride in a 3:1 ratio, available in powder (P) and ultrafine powder (UFP) grades, with an acid number of 265 to 305. SMA resins designated as LO are free of acetophenone, the main odor component of SMA Resins. SMA 10840 (Atofina Chemicals Inc.) is a copolymer of styrene and maleic anhydride esterified about 65% with iso-octanol, having an acid number of
about 240.

DSC Studies. Resin mixtures for DSC analysis were dry blended by grinding in a coffee mill for 5 minutes. The powders were analyzed on a TA Instruments DSC 2920 instrument, using a heating profile of 10°C/ min.

Powder coating formulations. All formulations are given in phr (parts-per-hundred resin), where the mass of "resin" (epoxy + polyester) totals 100 and all other ingredients are given as a fraction of this mass. Formulations were prepared on a 1-kg scale, with premixing via a "bag-shake," where the ingredients were simply shaken together in a bag. After premixing, the blend was passed through a lab-scale 50 mm twin-screw APV extruder. Unless stated otherwise, all formulations were prepared under high-shear conditions at 400 rpm with a rear-zone temperature of 100°F and a front-zone temperature of 175°F. After cooling, the resin blends were ground in a hammermill and passed through a 140 mesh (105 micrometer) screen. Test panels were sprayed using an electrostatic spray gun to a dry film thickness of 2.0 ± 0.2 mils and cured in an oven at 350, 375 or 400°F for 10 minutes; at 375°F for 15 minutes; or at 300°F for 20 minutes.

Physical testing. Panels were evaluated for 60-degree gloss, forward impact resistance, reverse impact resistance, crosshatch adhesion and solvent resistance. Gloss values were measured using a BYK Micro-Gloss 60-degree meter with a statistics feature; all reported values are the average of 10 readings. Impact resistance was measured using a Gardner impact tester and reported values are the highest level of impact at which the coatings showed no cracking. Solvent resistance was evaluated by rubbing a cotton ball soaked in methyl ethyl ketone (MEK) back and forth over the surface 50 times. After drying, the coating was inspected for any changes in appearance. A 'pass' rating indicates no visible change, while a 'fail' indicates that the film was completely removed. A rating of 'slight softening' was given when the coating became softer with a visible change in appearance. 'Softened' indicates more severe swelling, where a significant amount of the coating came off onto the cotton ball

the cotton ball.

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